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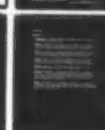
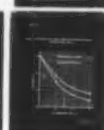
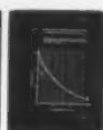
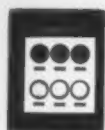
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DEVELOPMENT OF A NEW DETECTOR FOR OIL
IN WATER

NAVAL AIR PROPULSION TEST CENTER
TRENTON, NEW JERSEY

FEBRUARY 1975

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NAVAL AIR PROPULSION TEST CENTER

TRENTON, NEW JERSEY 08628

PROPULSION TECHNOLOGY AND PROJECT ENGINEERING DEPARTMENT

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FEBRUARY 1975

DEVELOPMENT OF A NEW DETECTOR FOR OIL IN WATER

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INTRODUCTION

Recent decisions to enforce the Federal Water Pollution Control Act amendments of 1972 have led to an urgent need for a sensitive, rapid and simple method for the determination of oil in water. Most current available laboratory and automated analytical techniques for oil detection depend on spectrometric or turbidimetric techniques which require considerable investments of equipment and trained personnel. An alternative economic field method, specifically designed for shipboard use, was therefore sought by the Naval Air Propulsion Test Center (NAPTC) in accordance with reference 1, authorized by the Naval Sea Systems Command (NAVSEA). The research effort led to the development of a new approach to the analysis of oil in water for which an invention disclosure has been submitted to the Department of the Navy (Navy Case Number 58661). This formal report presents the details of the design, operation and capabilities of the oil in water detection method. A report on preliminary work was included in reference 2.

CONCLUSIONS

1. A new approach to the analysis of oil in water was developed. The technique is applicable as a field detection method suitable for shipboard use.
2. The oil in water detector can be used for the quantitative analysis of undissolved particulate oil present in water over a zero to 30 parts per million (ppm) (v/v) concentration range.
3. The method is not sensitive to dissolved oils and the measurements are not influenced by the presence of surfactants which often are found in bilge water.
4. The method is rapid and can be performed by non-technical personnel. The final readout may be obtained either by simple visual color intensity matching or by means of a reflectance meter.

RECOMMENDATIONS

1. The oil in water detector should be developed into an efficient workable instrument and be distributed among Navy field activities for evaluation. The results obtained in the field should be compared to analysis of samples forwarded to chemical laboratories.
2. The new approach to the analysis of oil in water should be adopted as a laboratory tool by Navy Research and Development facilities engaged in the evaluation of oily water separators and monitors. The advantages gained by employing the new method are speed, high sensitivity and decreased investments of equipment and trained personnel.

3. Attempts should be made to eliminate the test variabilities due to extreme variations in oil product composition. A recommended experimental approach is to modify the composition of the dye and filtering element.
4. It is recommended that tests on the use of glass fiber filtering elements be continued and that attempts be made to design in-line sampling systems with capabilities for automatic filtering element processing and reflectance analysis.

DESCRIPTION

General Scheme of Detection Method

A technique was developed for the detection of small quantities of liquids of low water solubility and surface-activity, dispersed in water. More specifically, the method was designed for the rapid, quantitative analysis of undissolved particulate oil present in ship waste water in the zero to 30 ppm (v/v) concentration range. The measurements were not affected by the presence of surface-active agents (surfactants) and could be performed by non-technical service personnel.

The first step in the analysis was to pass a specified volume of the water sample through a filtering element at a prescribed flow rate. The undissolved oil droplets present in the water appeared to be retained by the matrix of the filtering element. The concentration of the retained oil on or near the upstream surface of the filtering element was then visualized by pressing the upstream surface against a dry surface which had been impregnated with an oil indicating material. The intensity of the stain developed in the filtering element was found to reflect the quantity of oil originally present in the water sample. The details of the material, apparatus and operations of the test procedure are described under the various headings below.

Filtering Element

Undissolved oil droplets dispersed in water were found to be effectively trapped by the matrix of filtering elements consisting of Millipore Absorbent Pads (Type AP10). The pads had a diameter of 1.85 inches, and a thickness of 0.03 inch and were made of white cellulose material resembling blotting paper. The pads are generally used in the laboratory as Millipore filter supports, for microbiological culturing, and to assist in the drying of Millipore filters.

Sampling Procedure

One Millipore absorbent pad was placed in a standard Millipore stainless steel filter holder and funnel. The filter holder was fitted to a 1-liter vacuum filtration flask. The filtration flask was attached to a vacuum-pressure pump (Millipore Type XX6000000). A 250 ml test sample of water

was poured into the funnel and allowed to flow through the filtering element by gravity. The filtration time should be 30 to 50 seconds and could be modified if necessary by means of vacuum application. Then, in order to partially dry the filtering element, air was drawn through the system for 20 seconds using a vacuum of approximately 17 inches of mercury. The filtering element was removed from the filter holder and placed in contact with a dry cellulose pad impregnated with oil indicating dye.

Dye Impregnated Pad

The white cellulose Millipore absorbent pads as described earlier were also used as the support vehicle for the oil indicating dye. The pads were submerged in a saturated ethanolic solution of Oil Blue B (E. I. DuPont de Nemours and Company) for three seconds. Upon removal from the solution, the pads were placed vertically in a rack and dried under vacuum at 85°C for 20 minutes. The dye impregnated pads were now ready for use and were kept stored in a desiccator.

Oil Visualization Method

After the filtration procedure, a dye impregnated pad was placed on the upstream surface of the filtering element. This combination of pads was then placed between two steel plates (each 2 X 2 X 0.25 inches) and the plates were clamped together under 3,000 pounds of pressure for two minutes by means of a hydraulic press. A press equipped with a pressure gauge (Fred S. Carver, Incorporated, Foundation Boulevard, Menominee Falls, Wisconsin) was required in order to standardize the pressure treatment and obtain accurate results. Upon completion of the compression period, the dye impregnated pad was discarded and the upstream surface of the filtering element was analyzed for a blue stain.

Quantification Techniques

The simplest method of estimating the oil concentration associated with a particular stain pattern was to compare the stain under white light to color photographs of a series of stain patterns produced by samples containing known oil concentrations as illustrated in Figure 1. The standards were carried through the normal analysis procedure. The oil concentrations used generally ranged from zero to 30 ppm (v/v).

A numerical value representing the intensity of the blue stain pattern could be obtained by means of reflection measurements. Percent reflectance was recorded by placing the Search Unit of a Photovolt Reflection Meter 670 (Photovolt Corporation, 1115 Broadway, New York) directly on the stained filtering element. The Search Unit was fitted with a green tristimulus filter and was calibrated before each reading by means of standard enamel plaques. A plot of known oil concentrations versus percent reflectance was constructed. The standard curve was then used to convert reflectance readings to oil concentrations. Figure 2 shown the plot of the reflectance readings obtained from the stained filtering elements reproduced in Figure 1.

Oil In Water Test Dispersions

In order to produce meaningful standard curves, relatively stable and homogeneous dispersions of known oil content had to be prepared for testing. Since the oil detection method was not influenced by surfactants, such agents could be used, together with vigorous mixing, to produce a uniform dispersion of the oil in water. Surfactant concentrations were employed which did not cause excessive foaming. Foams often are enriched in the solute and may thus greatly dilute the bulk solution. In order to reduce oil loss due to adsorption to glassware and other surfaces, the surfactant was always mixed with the water before the appropriate volume of oil was added. The following surfactants were used during the studies and were found not to interfere with the tests: Tween 80 and Span 80 (Atlas Chemical Industries, Incorporated), Tide (Proctor and Gamble), Zif Cleaner (Bestline Products, Incorporated), Industroclean (Amway Corporation).

DISCUSSION AND ANALYSIS OF RESULTS

Sensitivity Requirements For Oil In Water Detectors

The Federal Water Pollution Control Act, as amended in 1972, prohibits oil in waste water streams from ships within the 12 mile limit if such discharge causes a sheen upon the surface of the water. In a study conducted by the Coast Guard (reference 3), it was determined empirically that a visible sheen of oil was produced on the water adjacent to a Coast Guard Cutter when the oil content of the water pumped overboard reached between 20 and 30 ppm.

Permits to discharge oil at Naval fuel annexes are controlled by regulations set forth by the Environmental Protection Agency (EPA) (40 CFR 110). A recent report (reference 4) described details of a particular permit governing a 300,000 gallon annual water discharge at a Navy installation in Hawaii. It was noted that the maximum oil and grease concentration allowable in the waste water was only 5 ppm. These observations indicated that the methods needed for the effective monitoring of oil in waste water streams should at least be sensitive to zero to 30 ppm of undissolved particulate oil. A capability for higher concentrations is also desirable for evaluation of the magnitude of a pollution problem and for laboratory investigations.

Literature Survey: Potential Oil In Water Detectors For Shipboard Use

Some recent reports (references 4, 5, and 6) have reviewed the methods currently available for determining oil in water. From the literature it was clear that none of the techniques met the requirements for a shipboard oil in water detector. The most current technique of choice

for oil analysis in the field was found to be the Fram/Trace Oil Analysis Kit (reference 4). This technique, however, appeared to have a number of serious limitations. For example, up to one hour may be required to set up for an oil in water analysis. It also seemed questionable if the various technical manipulations involved could be successfully carried out in the field by average Navy field personnel.

New Oil In Water Detector: Sensitivity, Repeatability and Accuracy

The graph in Figure 2 illustrates the sensitivity of the detector to dispersed oil droplets in 250 ml water samples over the critical zero to 30 ppm range. It should be understood that the concentration range of maximum sensitivity in the present method can readily be shifted by simply using smaller or larger testing volumes. The reflectance versus concentration relationship shown in Figure 2 produced by 250 ml water samples was chosen in order to make the test method a tool useful for the determination of conformance with present pollution standards.

The repeatability of tests on laboratory-prepared known samples was found to be quite satisfactory. A typical example of the precision and accuracy of the method is shown in Table I. Reproducibility was found to depend to a large extent on the control of the following factors: the sample filtration rate, the extent of air drying of the filtering element, and the pressure and duration of the filtering element-dye pad compression.

The nature of the material making up the matrix of the filtering element appeared to govern the pressure required for maximum color development. Data from some preliminary studies indicated that good test responses could be obtained when glass fiber filtering elements (Millipore AP 20 filters) were substituted for the cellulose elements. The pressure requirement for maximum color development was found to be reduced by a factor of 100. Further investigation on the use of glass fiber filtering elements should therefore be conducted.

Test Variabilities Due to Oil Product Composition

The oil in water detector method appeared to depend on two basic processes involving the oil product composition: a) the adsorption of the oil onto the filtering element and b) the solubility of the dye in the oil. It should be noted that to be effective, the dye also had to be relatively insoluble in water and possess an intense color. In view of the basic mechanisms involved, it was necessary to establish that the indicating dye would dissolve in all the oil products likely to be present in a waste water sample. A study of the composition of oils found in over

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50 samples of ship bilges from destroyers at San Diego, indicated that the average composition was 75 percent lube oil and 25 percent fuel oil (reference 7). A survey of commercially available water insoluble dyes with near equal solubility in lube and fuel oils led to a number of useful materials. Among these were Oil Blue B (E. I. DuPont de Nemours and Company), Automate Blue Number 8 (Morton Chemical Company) and Oil Red O (Allied Chemical Company). The preferred dye used in the present detector was Oil Blue B. The standard curves plotted in Figure 3, however, showed that equal concentrations of lube and fuel oils gave somewhat different reflectance readings under the test conditions. The discrepancy could be due to a dye solubility problem and/or differences in the interactions of lube and fuel oil with the filtering element. The replacement of the cellulose filtering element with elements composed of glass fibers or polymeric materials such as Nylon, Teflon or polypropylene was found not to relieve this problem. It is hoped that the deficiency can be corrected or reduced by combining the present dye with an emulsifying agent or by the synthesis of a new dye with equal solubility in lube and fuel oils. It should be noted, however, that in Figure 3 the uncertainty of the oil concentration near the 10 ppm range associated with a reflectance reading from an unknown lube oil fuel oil mixture would only be about ± 1 ppm if a mean calibration curve were constructed.

FIGURE 1: STAIN PATTERNS FROM TESTS OF STANDARD DISPERSIONS
OF NAVY DISTILLATE FUEL OIL IN WATER

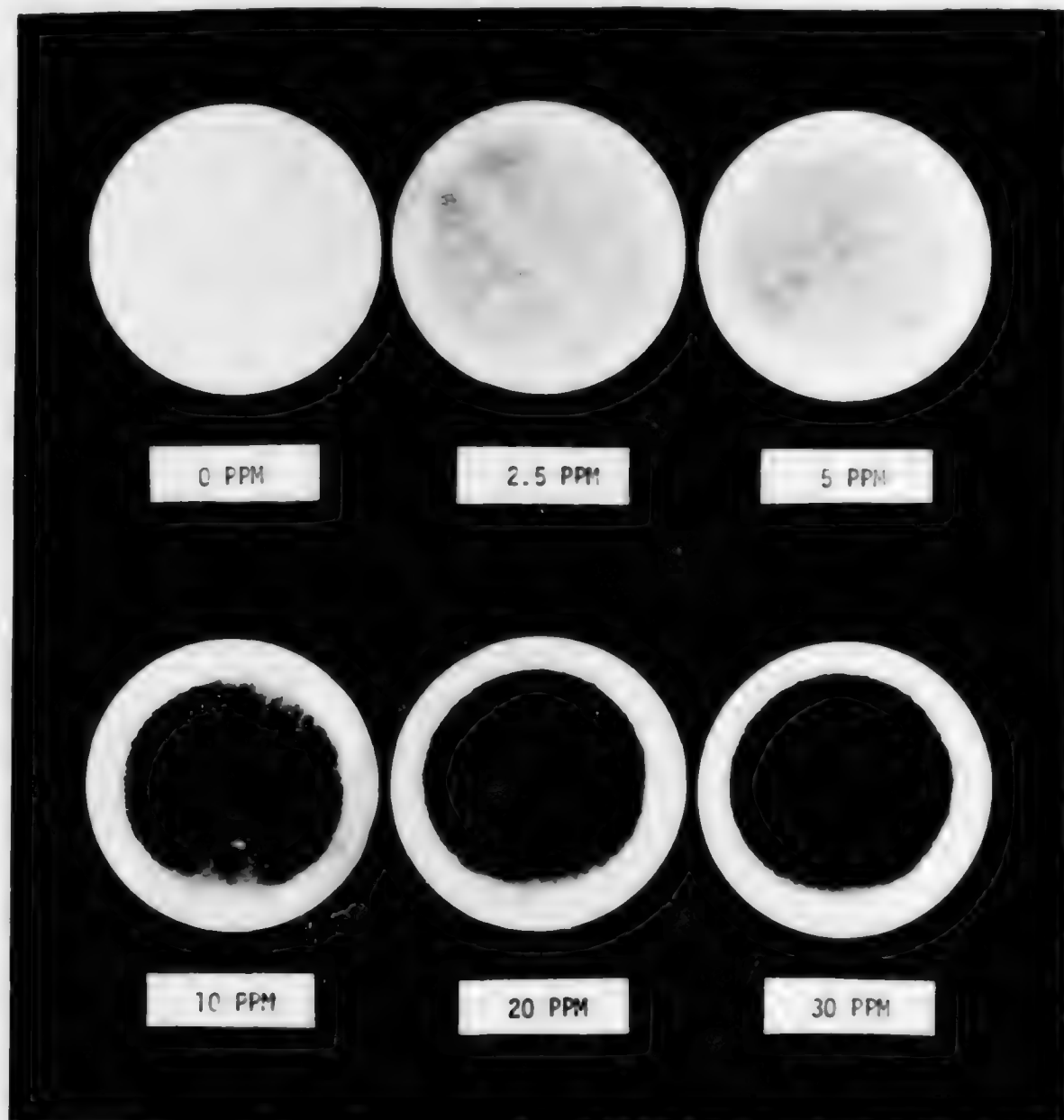


FIGURE 2: STANDARD CURVE FOR CONVERTING REFLECTANCE READINGS
TO CONCENTRATIONS OF NAVY DISTILLATE FUEL OIL

Reproductions of the actual filtering elements
from which the reflectance readings were obtained
are shown in Figure 1.

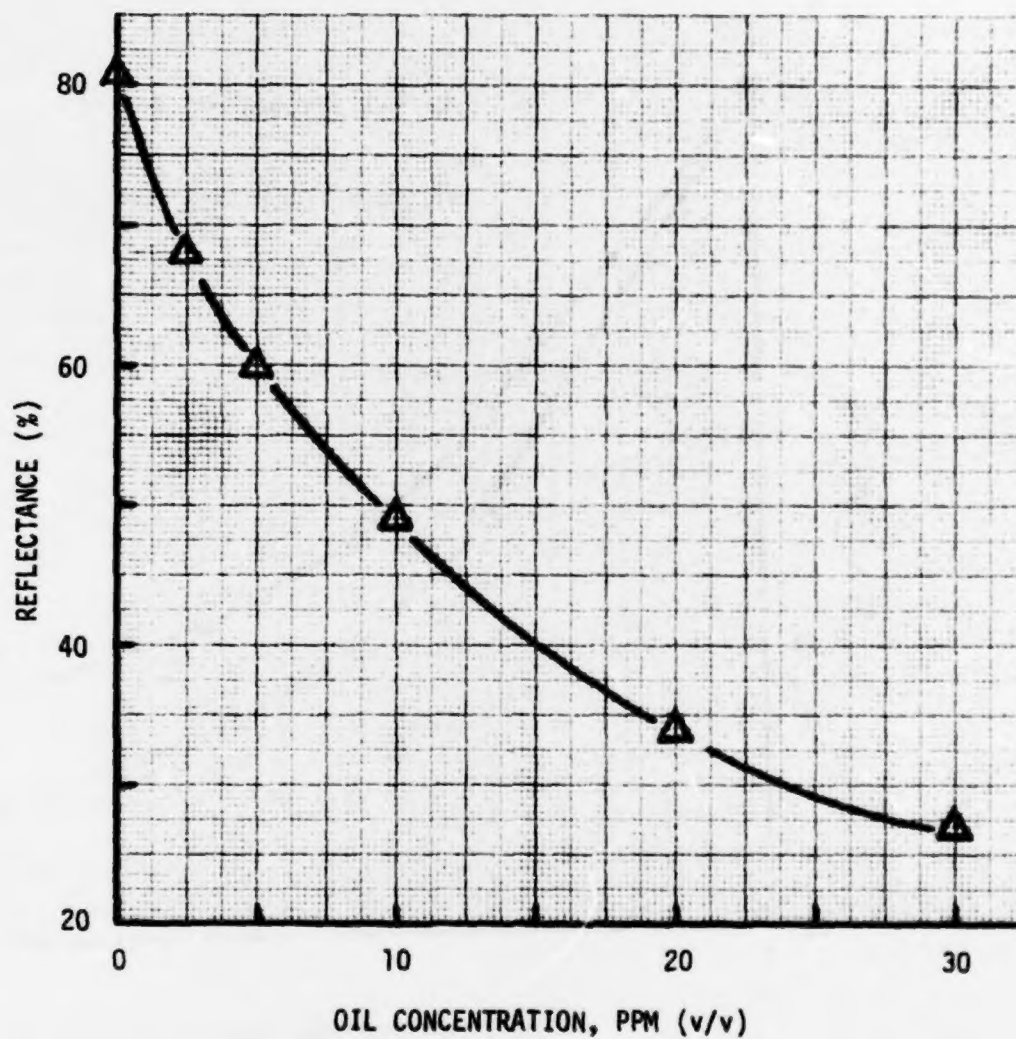


FIGURE 2

FIGURE 3: THE INFLUENCE OF OIL PRODUCT COMPOSITION ON REFLECTANCE READINGS:
LUBRICATING VERSUS FUEL OIL

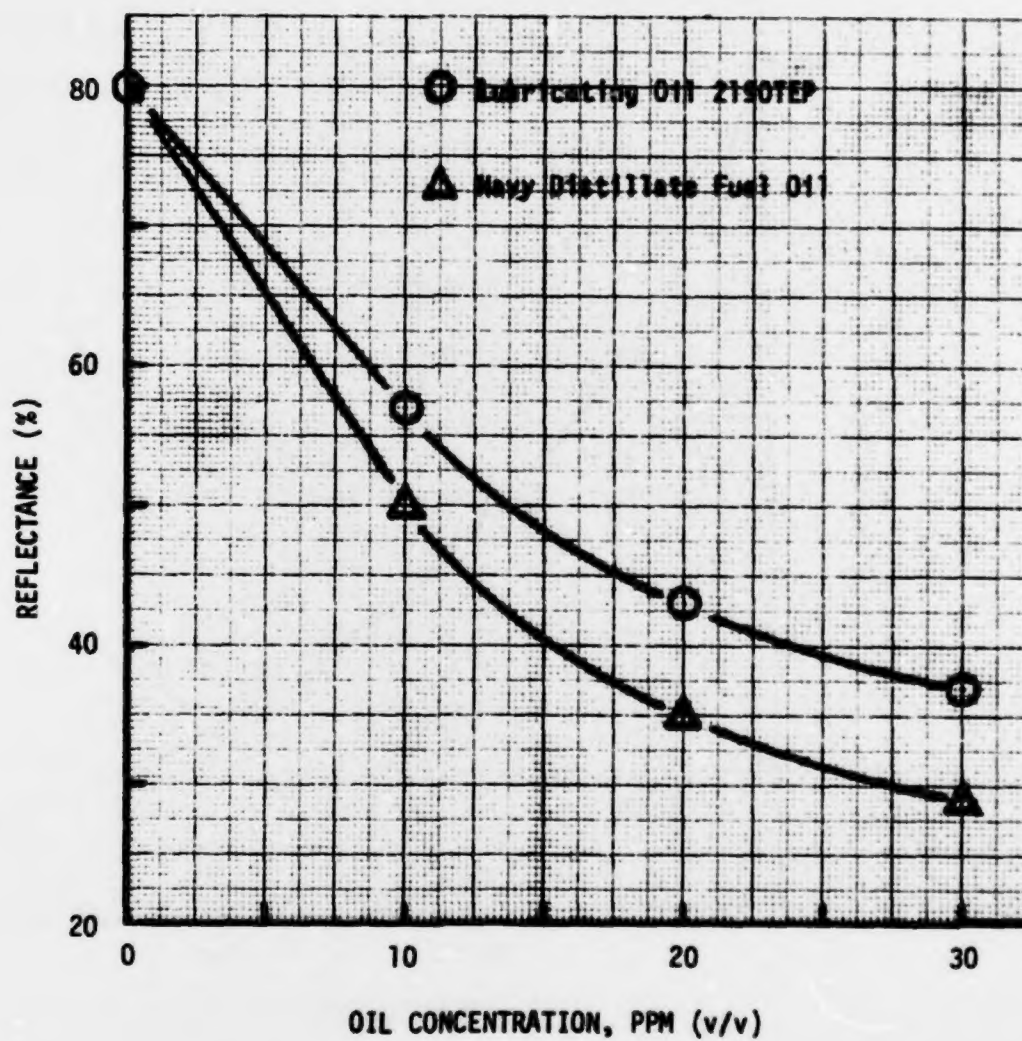


FIGURE 3

TABLE I

STATISTICAL ANALYSIS OF REFLECTION MEASUREMENTS FROM TESTS OF FIVE SEPARATE
SERIES OF LUBRICATING OIL (2190TEP) DISPERSIONS IN WATER

<u>Series No.</u>	<u>REFLECTANCE (%)</u>			
	<u>0 PPM oil</u>	<u>10 PPM oil</u>	<u>20 PPM oil</u>	<u>30 PPM oil</u>
1	78	56	43	38
2	80	57	43	37
3	79	54	45	36
4	79	56	44	34
5	81	57	46	38
Mean Value	79.4	56.0	44.2	36.6
Standard Deviation	<u>+1.1</u>	<u>+1.2</u>	<u>+1.3</u>	<u>+1.7</u>

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